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CERAMIC MIXTURES WITH DECREASED POROSITY FOR DECORATIVE MAJOLICA

N. S. Yugai[1] and V. M. Loginov[1]

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Ceramic mixtures of low porosity were developed on the basis of poorly sinterable clay from the Gzhel' deposit with part of it mechanically activated, as well as nepheline-sienite and cullet additives. The introduction of cullet to clays of different dispersion levels made it possible to decrease the firing temperature and to shorten the process of majolica production, due to one-time firing.

Low-temperature ceramic mixtures used in production of household and artistic majolica articles represent a composition of low-melting clays and various additives.

The local clays used at the Gzhel' Production Association belong to the group of poorly sintering clays and are characterized by instability of the chemical, mineralogical, and granulometric composition. The elevated porosity of Gzhel' majolica products is their main drawback.

It is known that the introduction of combined fluxes in the form of nepheline-sienite, perlite, or each additive separately into ceramic mixtures leads to decreased porosity of ceramics and decreased firing temperature. Furthermore, the use of a combination of clays with different degrees of dispersion and mineralogical compositions decreases water absorption as well, although these clays separately can have high porosity [1].

In order to sinter the mixture made from poorly sinterable clay from the Voronovskoe deposit, the study in [2] determined the favorable values of the ratio $RO : R_2O$ (0.5 – 1.0), as well as their sum, equal to 10 – 11%.

By their chemical composition, the clays from the Gzhel' deposit in their natural form are not suitable for the production of majolica articles (Table 1). According to Avgustinnik's diagram [3], clays suitable for majolica production have a ratio of the mass content $Al_2O_3 : SiO_2$ equal to 0.18 – 0.25, and a total mass content of fluxes $(RO + R_2O + Fe_2O_3)/100$ equal to 0.08 – 0.17.

In developing majolica mixtures with decreased porosity based on a combination of clays with different degrees of dispersion, the main material, i.e., the variegated-color clay from the Gzhel' deposit, was subjected to mechanical activation. As a consequence of wet milling and sieve concentration of the clay, the content of the fine-disperse fraction (up to 1 μm) increased by 10% compared with unmilled clay (Table 2). It was found that an increase in the milled clay

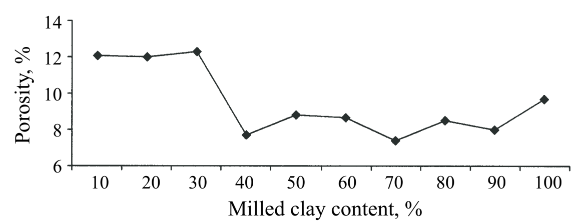

Fig. 1. Dependence of the porosity of mixtures in air-dry state on the milled clay content.

[1] Gzhel' Production Association, Vladimir Region, Russia.

TABLE 1

Clay from Gzhel' deposit	Mass content, %								$Al_2O_3 : SiO_2$	$\frac{RO + R_2O + Fe_2O_3}{100}$
	SiO_2	$Al_2O_3 + TiO_2$	Fe_2O_3	CaO	MgO	Na_2O	K_2O	calcination loss		
Variegated	56.62	19.54	8.41	2.73	1.39	0.33	6.86	5.00	0.345	0.20
Green	58.40	22.27	5.73	1.82	1.92	0.29	5.53	4.40	0.381	0.15
Gray	63.92	18.08	5.37	1.27	1.82	0.24	5.68	3.78	0.282	0.14
Lilac	60.38	19.15	8.05	1.09	1.72	0.41	4.98	4.10	0.317	0.17
Gray-green	63.36	18.34	5.37	1.27	1.98	0.30	5.46	3.90	0.289	0.14

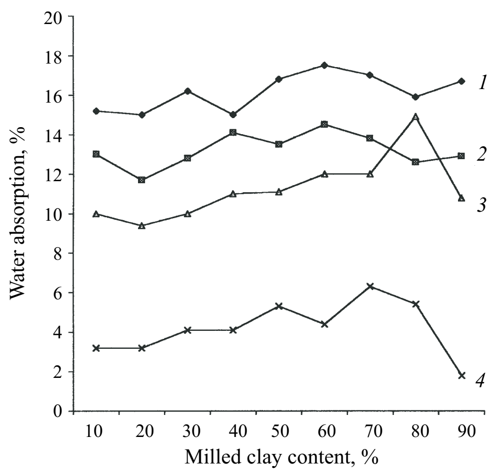

Fig. 2. The effect of milled clay on mixture porosity at firing temperatures 900 (*1*), 950 (*2*), 1000 (*3*), and 1050°C (*4*).

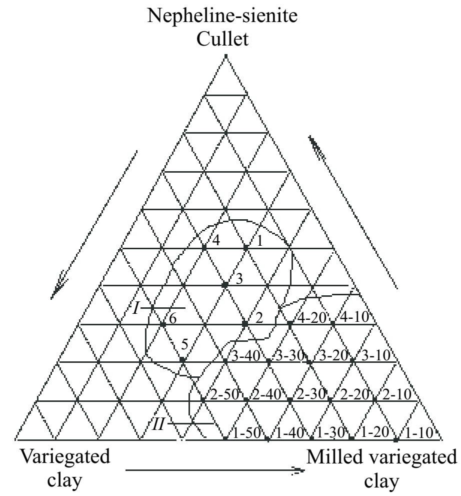

Fig. 3. Phase diagram of majolica mixture compositions with nepheline-sienite (*I*) and cullet (*II*).

TABLE 2

Clay from Gzhel' deposit	Content of particles, %, of size, μm					
	< 1	1 – 5	5 – 10	10 – 20	20 – 40	> 40
Variegated:						
before milling	39.5	26.5	13.5	9.5	11.0	–
after milling	49.0	33.0	14.0	4.0	–	–
Green	27.5	40.5	19.0	13.0	–	–
Gray-green	30.0	31.0	20.0	14.0	1.5	3.5

TABLE 3

Mixture composition	Plasticity	Shrinkage, %, at firing temperature, °C					Mechanical strength, MPa	
		800	850	900	950	1000	in air-dry state	at temperature 1000°C
1	4.2	0.5	0.2	0.5	2.1	2.8	5.5	24.9
2	3.3	0.7	0.03	0.8	3.6	7.0	6.6	50.8
3	3.9	0.8	0.5	0.7	3.3	5.4	6.3	51.3
4	4.2	0.4	0.2	0.1	1.5	3.3	6.2	32.5
5	4.3	1.0	0.8	0.8	2.8	3.7	6.2	32.4
6	4.0	0.6	0.5	0.6	3.1	4.8	6.2	32.4
1-10	4.8	2.3	2.5	2.4	2.4	2.3	6.2	34.9
2-10	4.9	2.3	1.6	2.1	0.8	2.2	7.8	34.7
3-10	3.6	2.4	2.1	2.0	2.0	2.2	6.8	33.9
4-10	4.8	2.3	2.5	2.4	2.4	2.3	6.2	35.7
1-20	4.2	0.3	1.1	3.4	2.4	1.7	5.1	39.2
2-20	4.4	1.5	0.9	2.7	3.9	4.5	5.0	38.0
3-20	4.4	1.6	1.1	4.1	4.5	4.9	4.7	38.6
4-20	4.8	0.3	0.9	2.7	1.7	4.1	4.6	39.1
1-30	6.0	0.5	1.4	3.1	3.2	3.6	6.1	35.7
2-30	4.7	0.8	0.9	1.7	3.3	3.5	5.7	39.3
3-30	4.7	1.9	3.2	4.3	4.4	4.6	5.9	53.1
1-40	4.8	1.5	2.7	3.5	3.8	4.3	5.7	64.5
2-40	5.2	2.1	3.6	4.0	5.5	5.6	5.5	67.8
3-40	5.0	2.6	4.4	5.2	5.8	5.9	5.9	61.4
1-50	3.5	3.0	3.6	4.6	4.9	7.2	5.3	45.2
2-50	3.8	2.3	4.2	4.9	5.9	7.1	4.7	38.6

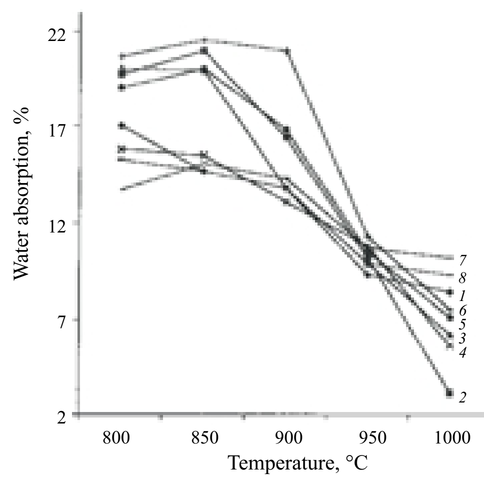

Fig. 4. The effect of nepheline-sienite on porosity of mixtures 1 – 6 (*1* – *6*), initial variegated clay (*7*), and milled variegated clay (*8*).

content from 10 to 90% leads to a modification of porosity in the air-dry state. As can be seen from Fig. 1*a* sharp decrease in porosity (from 12 to 7%) is registered for milled clay content equal to 40% and 70%. As the milled clay content grows from 40 to 70%, and from 80 to 90%, the porosity increases insignificantly (up to 9%).

Consequently, it is possible to accomplish dense packing of a ceramic mixture in an air-dry state by means of using a combination of clays which are of the same variety, provided that part of this clay had been subjected to mechanical activation.

Thus, the porosity can be decreased by adding 10 – 30% mechanically activated clay to the mixture.

In studying the effect of nepheline-sienite on the mixture sintering process, the water absorption was determined for samples (tiles) fired at maximum temperatures of 800, 850, 900, 950, 1000, 1050, and 1100°C with 30 min exposure at the final temperature (Figs. 3 and 4).

After firing at temperatures 800 and 900°C, the mixtures with nepheline-sienite had significantly larger porosity than the Gzhel' clay mixtures. Depending on the composition of mixtures with nepheline-sienite, an abrupt decrease in the water absorption (3 – 8%) was registered in the temperature range of 950 – 1000°C. The required degree of sinterability in the mixture based on variegated clay from the Gzhel' deposit with nepheline-sienite was reached at temperature 1000°C, the ratio $RO : R_2O$ being equal to 0.25 – 0.33 and the sum $RO + R_2O$ equal to 14.6 – 20.0.

It should be noted that when nepheline-sienite is replaced by cullet (10 – 30%), the start of the mixture sintering is shifted toward lower temperatures (below 900°C). The mixtures containing 40 and 50% cullet sinter at a temperature as low as 800°C. Their water absorption is 4.1 – 8.0% (Fig. 5).

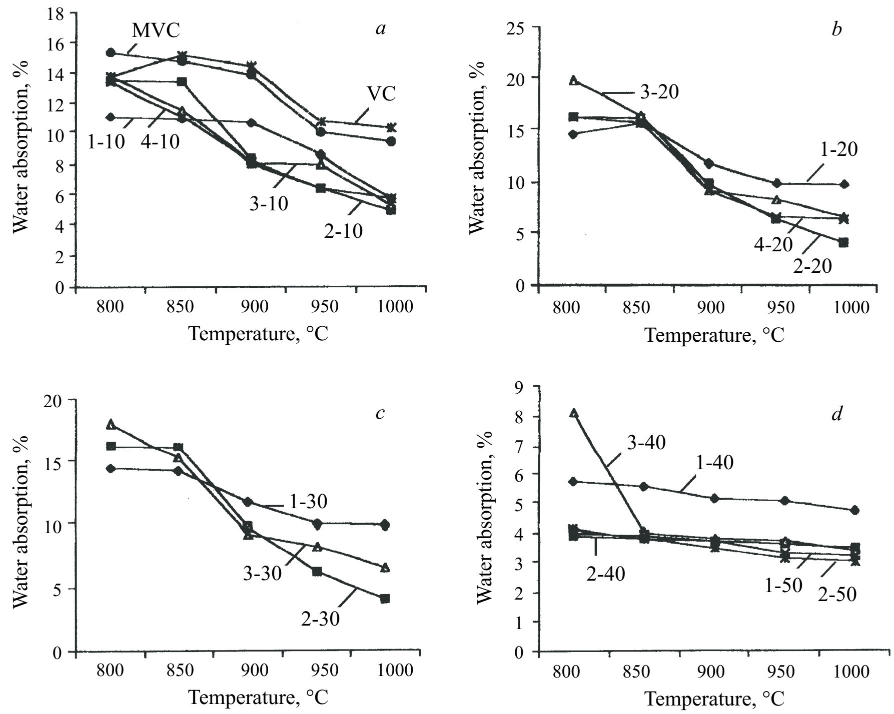

Fig. 5. Dependence of water absorption of mixtures on adding 10% cullet and 10 – 30% milled clay (*a*), 20% cullet and 10 – 30% milled clay (*b*), 30% cullet and 10 – 30% milled clay (*c*), and 40 – 50% cullet and 10 – 20% milled clay (*d*). Curve numbers correspond to mixture compositions; VC) variegated clay; MVC) milled variegated clay.

As the firing temperature increases, a relationship between the porosity and the milled clay content is observed in mixtures with glass cullet and a combination of clays. At low firing temperatures, (800°C), the effect of the milled clay on decreasing porosity is not very perceptible, but with increasing firing temperature, the porosity decreases proportionally to the increasing share of milled clay in the mixture composition. Furthermore, it was found that at temperature 900°C, the porosity values of all mixtures containing milled clay and cullet (10, 20, and 30%) coincide.

A distinctive feature of the mixtures with cullet is their low porosity (up to 6%) in the temperature interval of 950 – 1000°C. A perceptible decrease in porosity is identified at temperature 900°C, especially in the mixtures with fine-disperse (milled) clay.

The compositions and the physicomechanical properties of the mixtures are shown in Fig. 3 and in Table 3.

Based on the obtained data, cullet-containing mixture 3-20 was selected for production testing. This mixture can be recommended for the production of majolica by the pottery method or plastic molding, with single-stage or two-stage firing within the temperature interval 850 – 950°C.

Thus, it is possible to decrease the porosity of ceramic mixtures based on Gzhel' clay, which has poor sinterability, by means of introducing 40 and 70% mechanically activated (milled) clay to the mixture composition, as well as by using clay with different levels of dispersion together with nepheline-sienite additives, in which the ratio $RO : R_2O$ should be within the limits of 0.25 – 0.33, and the sum $RO + R_2O$ should be equal to 14.6 – 20.0. Furthermore, by adding cullet to mixtures based on clays of different dispersion levels, it is possible not only to decrease the porosity and bring the firing temperature down to 900°C, but also to shorten the technological process, due to one-stage firing. Complete sintering will be ensured in this way.

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